



U.S. Department of Energy Energy Efficiency and Renewable Energy

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Hydrogen, Fuel Cells & Infrastructure Technologies Program

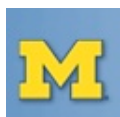
Materials in the DOE Hydrogen Sorption Center of Excellence

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National Renewable Energy Laboratory

Partners: 9 universities, 5 government labs, 1 company



AIR
PRODUCTS



PENNSTATE





- **Overview of sorption center:** objectives and strategy, partners, research cluster organization.
- **Engineered nanospace:** High surface area, porous high-density materials.
- **Substituted materials:** Heterogeneous materials with enhanced H₂ binding energies.
- **Strong binding:** Metal decorated materials with strong H₂ metal interaction.
- **Spillover:** Catalytic hydrogen dissociative adsorption.
- **Conclusions**



Objectives

Discover and develop high-capacity sorbent materials that can operate at ambient temperatures and be efficiently and quickly charged on-board with minimum energy requirements and minimum penalties to the hydrogen fuel infrastructure. Overcome barriers to 2010 DOE system goals and identify pathways to meet 2015 goals.

- Optimize sorbent material with high surface area and high density to meet both gravimetric and volumetric targets simultaneously with rapid kinetics.
- Develop materials which utilize mechanisms that bind H_2 with an optimal energy for near ambient operation (10 - 20 kJ/mol H_2).
- Devise facile synthetic routes using low cost approaches.

DOE 2010 Technical Targets for Storage System

- Gravimetric 0.06 kg H_2 /kg
- Volumetric 0.045 kg H_2 /L



Tuning Sorption Materials to Meet Both Volumetric and Gravimetric Targets

Volumetric capacity versus gravimetric capacity:

Specific Number of Sorption Sites: $D_s = N_s / M = S_{SSA} / s_0$

Gravimetric Capacity: $C_W = N_s n_H / M = D_s n_H$

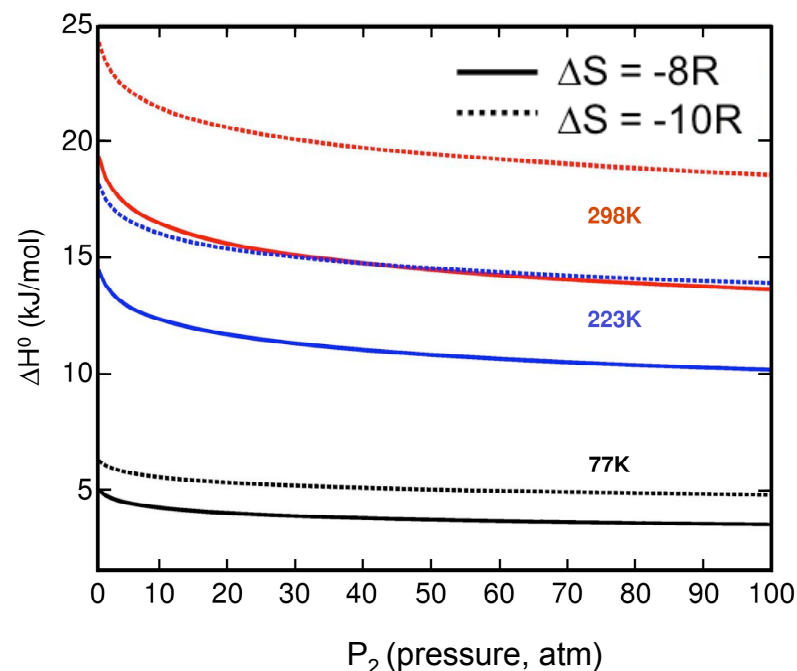
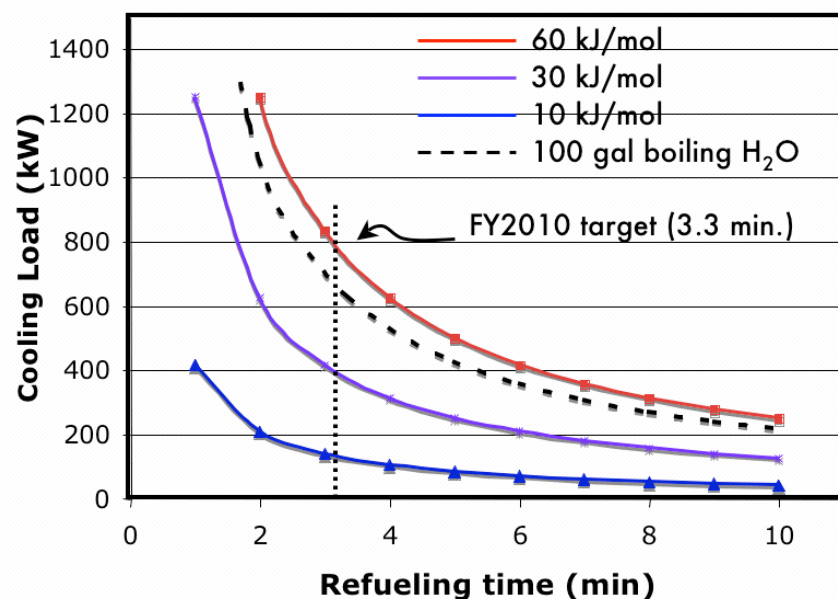
Volumetric Capacity: $C_V = D_s n_H D_M = C_W D_M$

N_s : Number of sorption sites
 M : Mass of the material
 S_{SSA} : Specific Surface Area
 s_0 : Area per sorption site
 n_H : Number of H atoms per site
 D_M : Density of the material

- **Volumetric capacity is proportional to both gravimetric capacity and *material density*.**
- **Increasing volumetric capacity and gravimetric capacity simultaneously requires increasing both high specific surface area and high packing density, which means larger pores should be avoided.**
- **An optimized system with 3.2 Å pore size and SSA + 11500 m²/g will enable 6 wt% and 50 kg/m³ hydrogen storage.**



Tune Binding Energy for Adsorption at Moderate Temperature and Pressure



- Heat removal with loading 5 kg of H₂ adversely impacts system capacities (heat exchangers) and refueling rates.
- The enthalpy should be the absolute minimum required to store the hydrogen.
- Sorbent materials offer the highest round trip (charge/discharge) energy efficiencies.

$$\Delta H_{\text{opt}} = T\Delta S + RT \ln(P_1 P_2 / P_0)$$

Charge to P₂ and discharge to P₁ (1.5 atm)
Entropy values for theoretical slit pore (-8R) and intercalated graphite (-10R).

After Bhatia & Myers, *Langmuir* **2006**, 22, 1688.

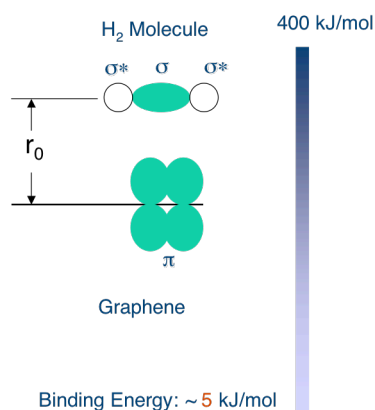


Research Clusters (RCs) Focused on Volumetric Packing and Designed Sorption Mechanisms

Research Clusters

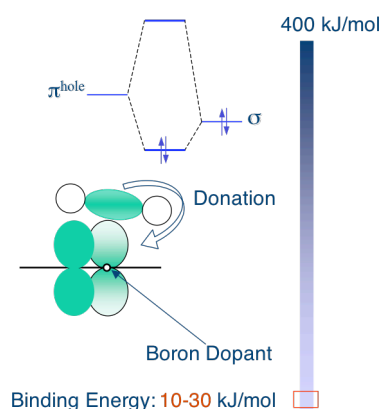
- **RC1: Engineered Nanospaces:** optimize material density and surface area.
- **RC2: Substituted Materials:** e.g. BC_3 to enhance binding energy.
- **RC3: Strong Binding:** stronger interaction with atomic metal atoms.
- **RC4: Spillover;** catalytic dissociative adsorption.

RC1



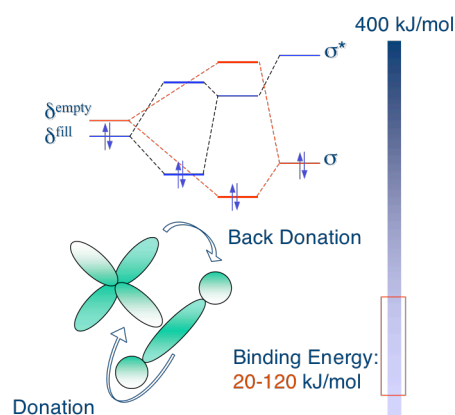
Physisorption

RC2



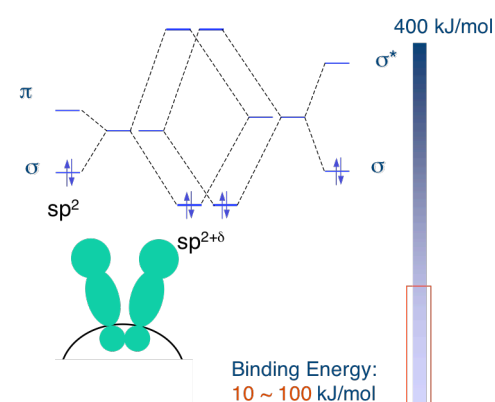
One-way Donation

RC3



Kubas

RC4



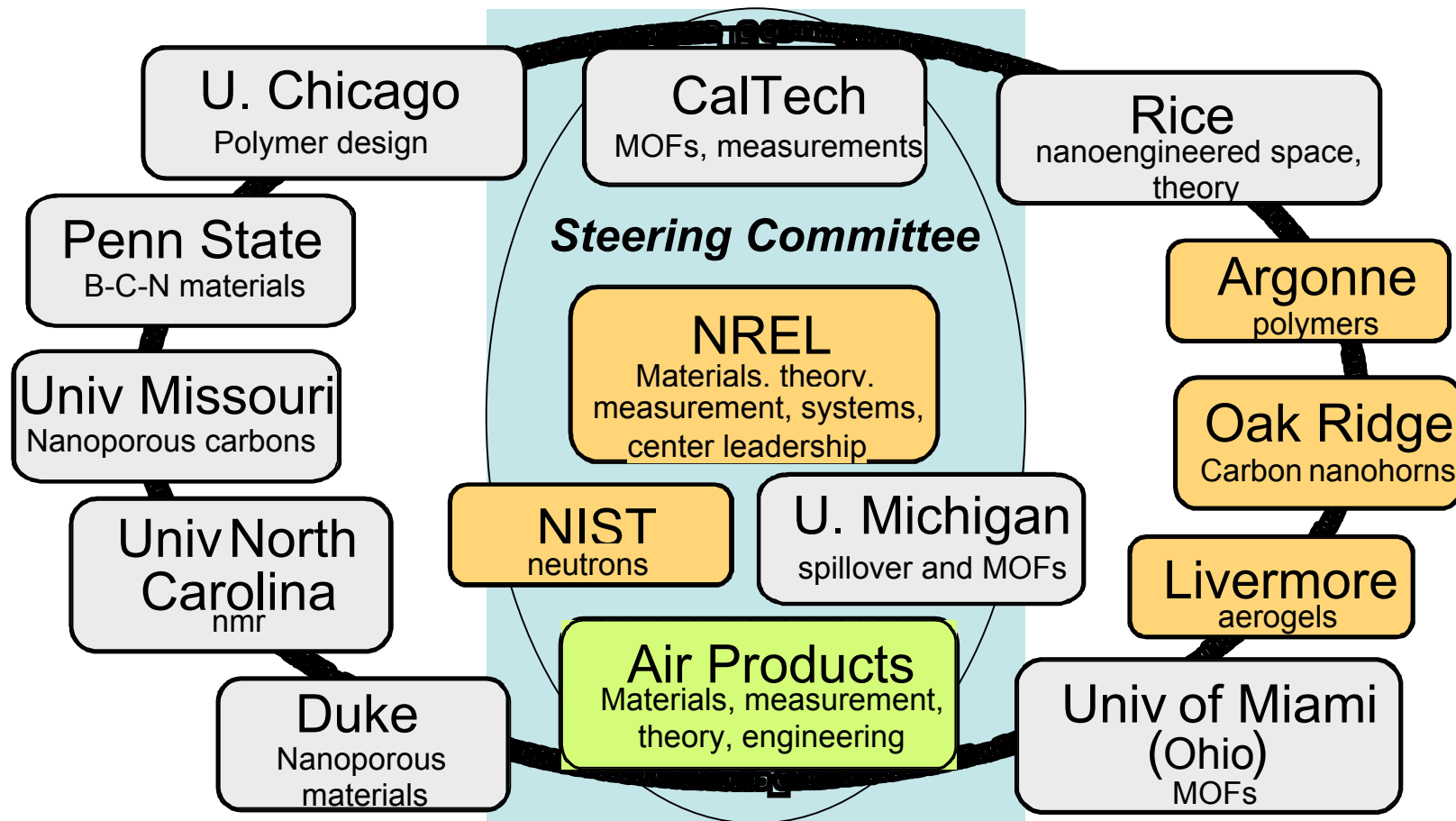
Weak Chemisorption
"spillover"



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Research Activities



□ University

□ Industry

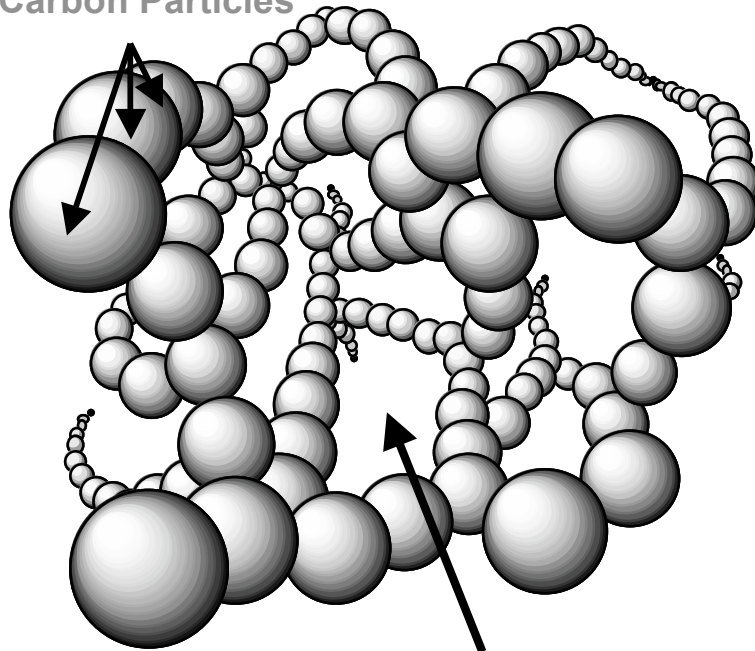
□ Federal Lab

9 universities, 5 government labs, 1 industrial partner

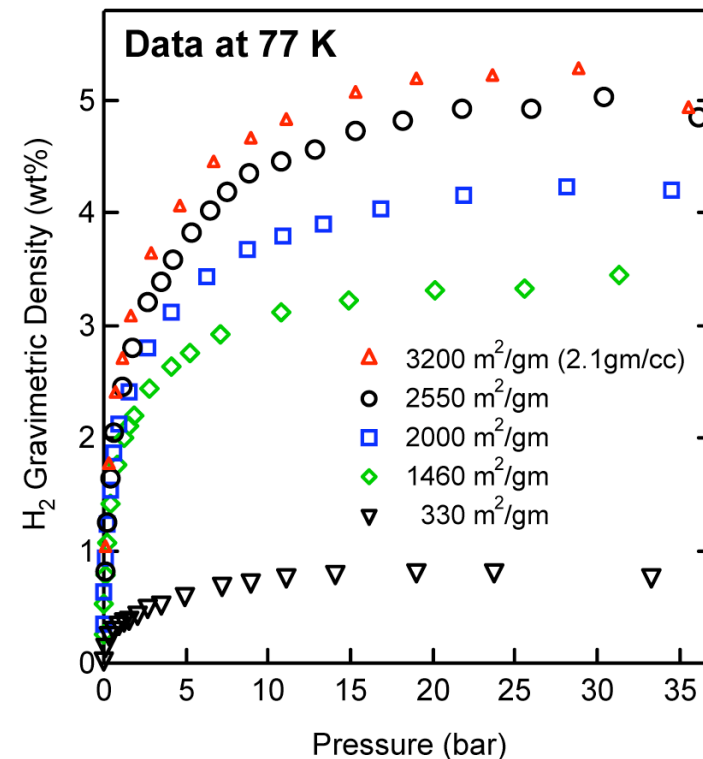


Carbon Aerogels for H₂ Sorption

Interconnected
Carbon Particles



Continuous Porosity



Kabbour, Baumann, Satcher, Saulnier and Ahn, *Chem. Mater.* **2006**, 18, 6085.

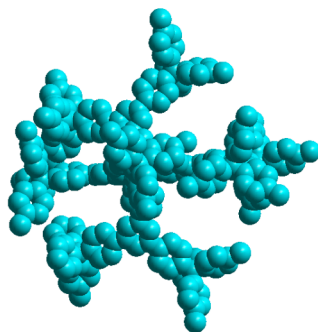
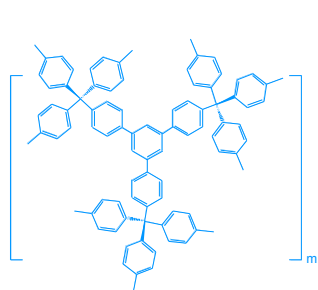
5.3 wt% and 0.029 kg H₂/L

- CA synthesis allows for control over bulk properties: **surface area, pore size, pore volume, density**.
- Homogeneous incorporation of **metal catalysts** is also possible.

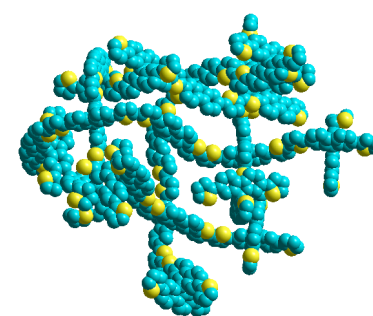
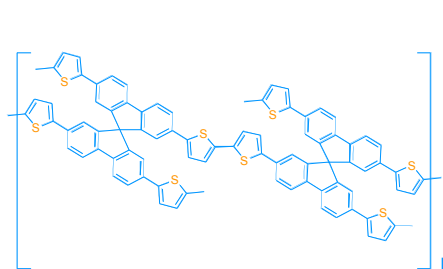




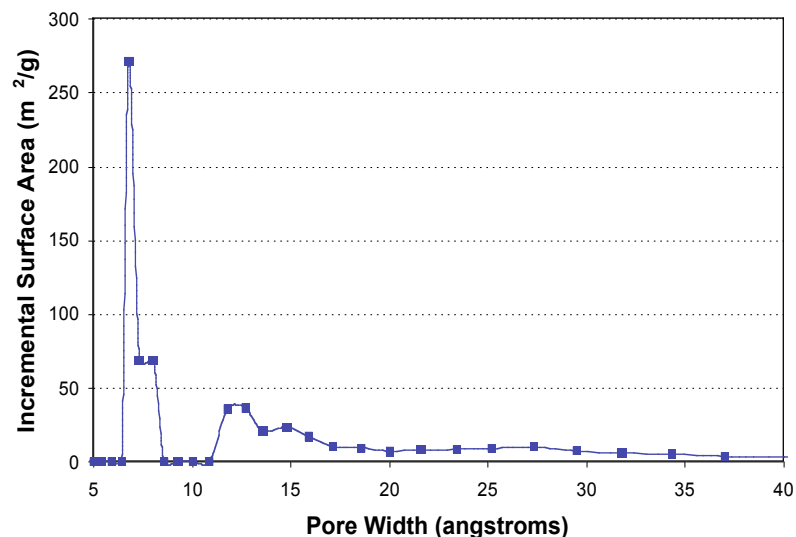
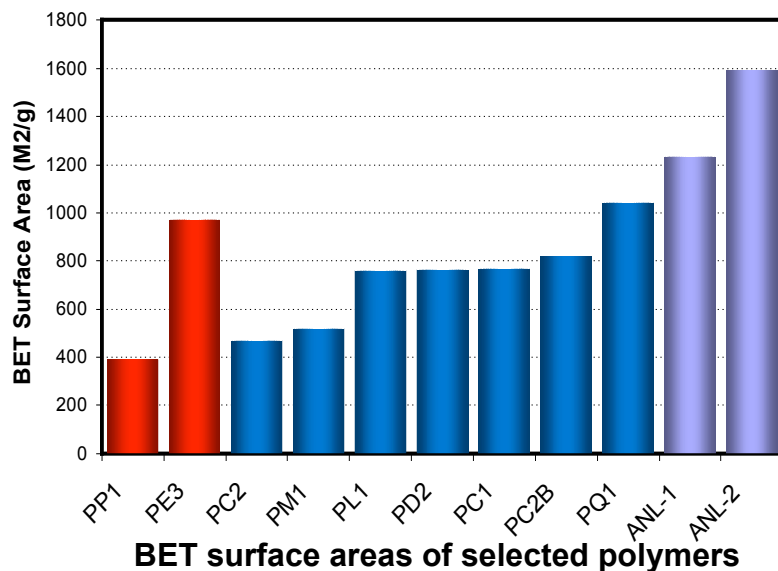
Nanostructured Polymers as Hydrogen Storage Media



Aromatics linked by tetraphenylmethane core



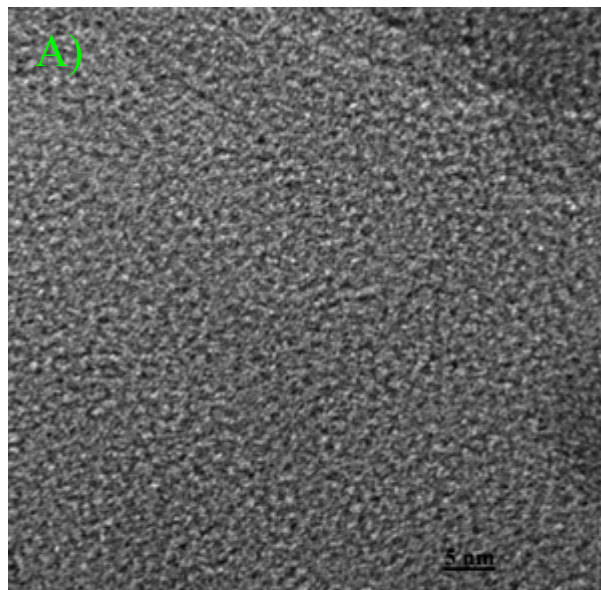
Conductive strand linked by spirobifluorene core



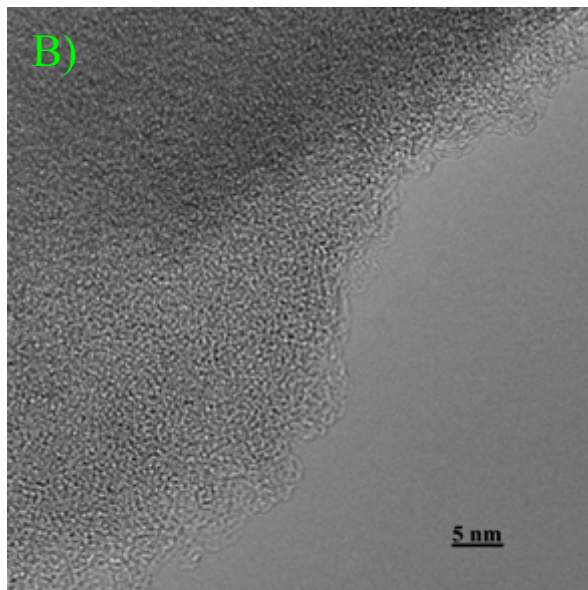
High surface areas / narrow pore distributions: 4.4 wt% and 0.034 kg/L



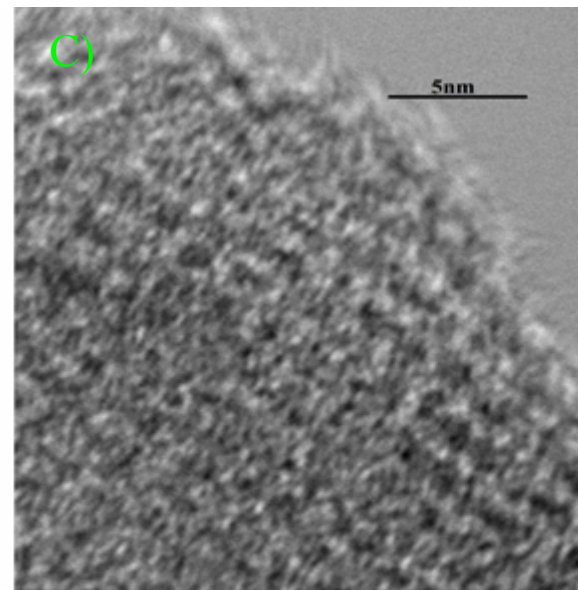
Microporous Carbons With Controlled Pore Sizes



1-2nm



1nm



0.6-0.8nm

- Surfactant molecules to form micelles with different sizes.
- Polymer precursor introduced interacts with the outer surface of the micelles.
- Polymerization results in a strong framework using micelles templates.
- Surfactants are thermally removed and polymer is graphitized to form desired matrix
- Process allows for tailored pore size and surface areas from 500-3000 m²/ g.
- Typically 1 wt% H₂ is absorbed / 500 m² surface area. (Chahine's Rule).





Microporous Carbons With Controlled Pore Sizes

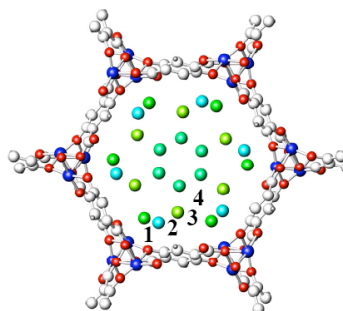
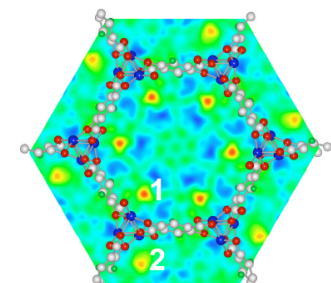
Four H₂ Binding Sites

Distances

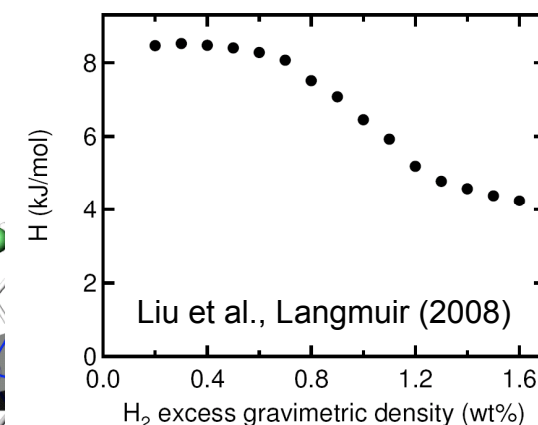
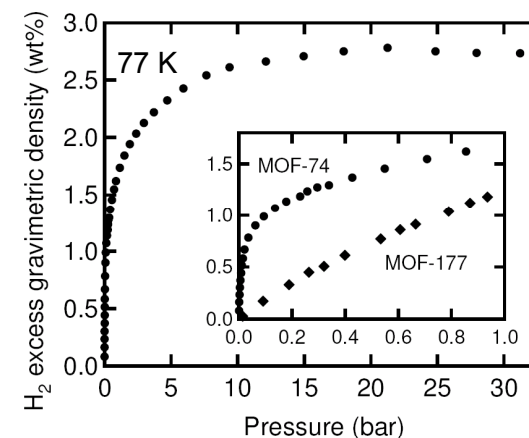
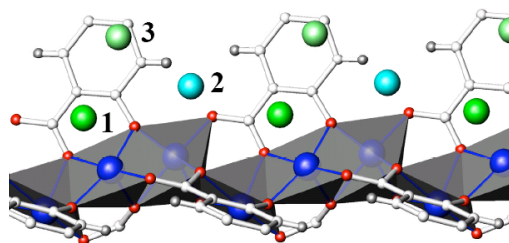
- Zn-H₂ : ~ **2.6 Å**
- H₂ @ site 1 to 2: ~ **2.9 Å**
- H₂ @ site 1 to 3: ~ **2.85 Å**
- D₂-D₂ in solid: ~ **3.6 Å**
- Close-packed H₂ layer on graphite: **3.51 Å**

Zn-based MOF-74

High initial enthalpy due to interaction with coordinatively unsaturated metal centers



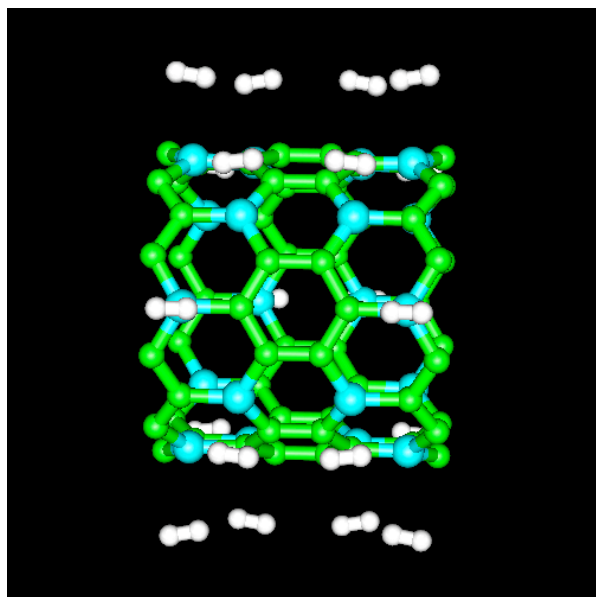
b)



- **First observation of denser packing than hydrogen monolayer**
- **Implications for enhanced H₂ packing and improvements in volumetric performance.**

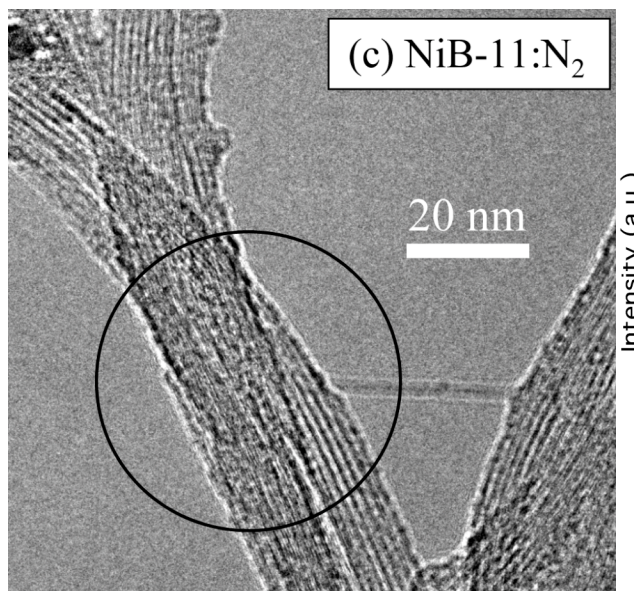


Boron-substituted Graphitic Materials for Enhanced H₂ Binding



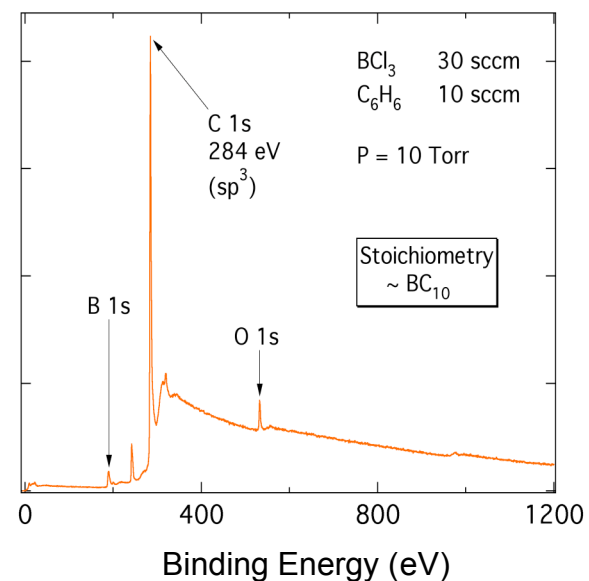
Enhanced H₂ binding
energy at boron site
(12-30 kJ / mol)

Kim et al., PRL 96, 16102 (2006)



Loading in laser-
generated carbon
nanotubes only 1-2 at.%

Blackburn et al., Chem. Mater. 18, 2558 (2006)



Have achieved ~9 at.%
loading in CVD thin films

Boron atoms predicted to bind H₂ with higher binding energy.
Boron incorporation depends on material and synthesis method.





Boron-loaded Highly Porous Carbons via Pyrolysis

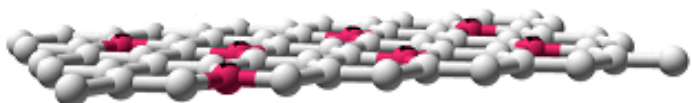
600 °C



1000 °C



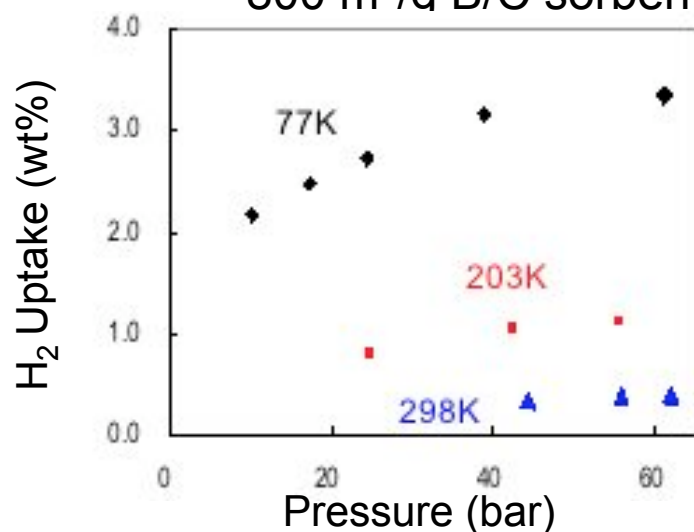
>1500 °C



- ~8 at% B from pyrolysis of polymers
(*NIST prompt gamma analysis*)

- B content decreases with pyrolysis temp.

~800 m²/g B/C sorbent

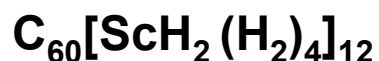
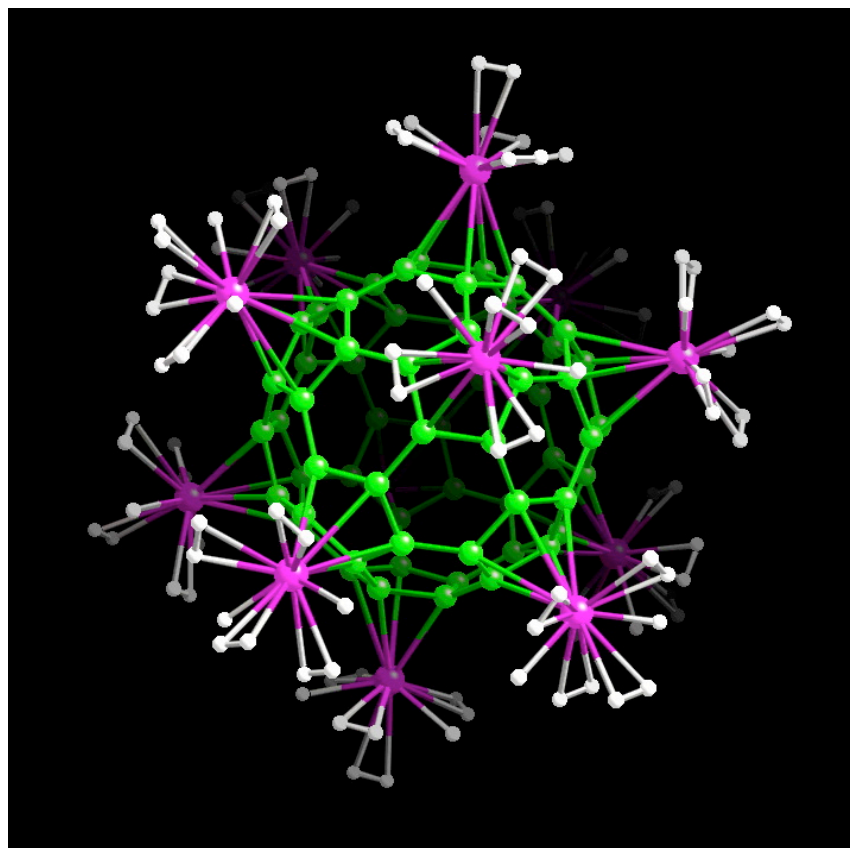


- B-doped materials store 2-3 times more H than activated carbon on a per SSA basis at both 77 K and RT. Data is for a B/C sorbent with a surface area of ~800 m²/g.





H₂ Binding via Kubas Interaction with Transition Metal



Organometallic Fullerenes

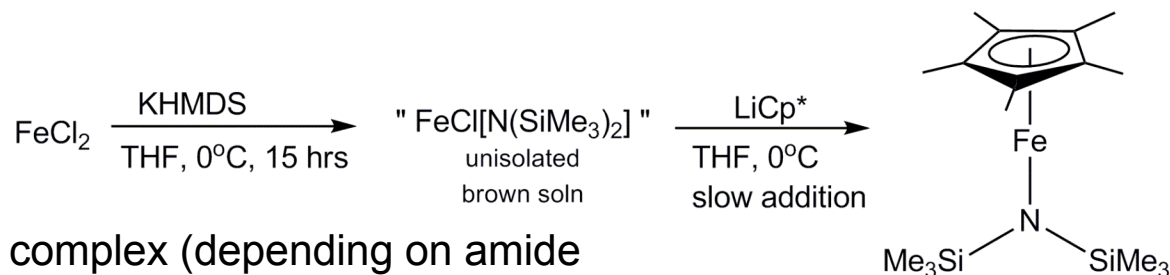
This theoretically stable Scandium organo-metallic complex represents a compound that stores hydrogen at 8.8 wt% with 7.0 wt% stored reversibly.

Minimum Energy Structure with regions around the 5-membered rings that have aromatic character.

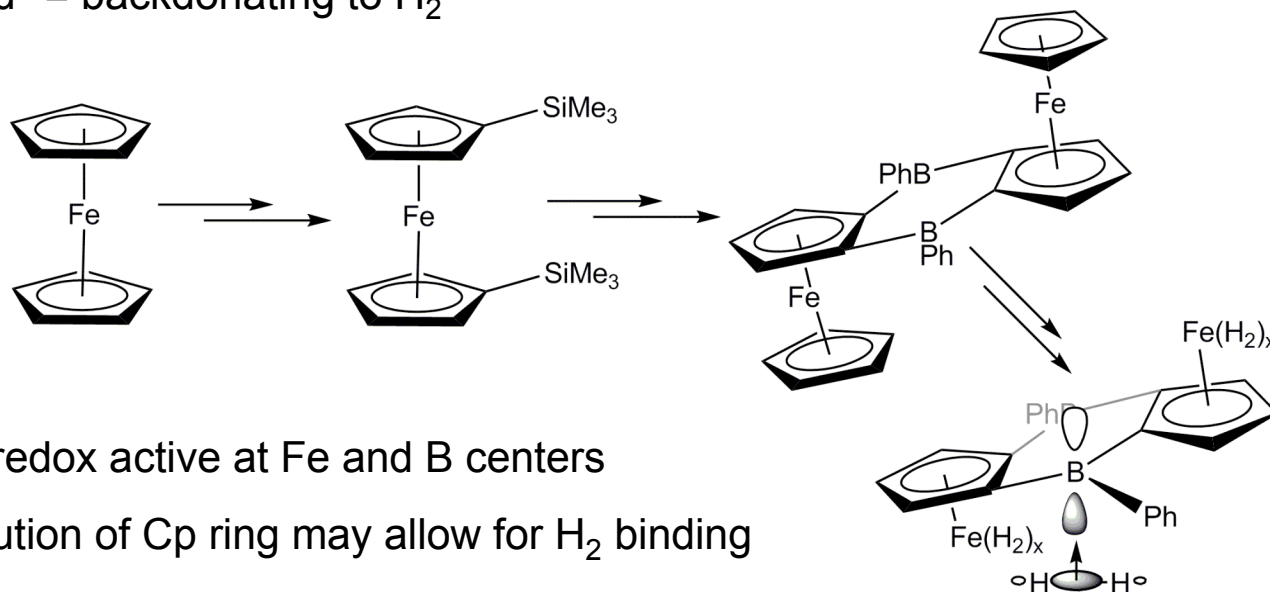
C₆₀ previously had aromatic character around the 6-membered rings. J. Poater, M. Duran and M. Sola Int. J. Quant. Chem. 98 (2004) 361.



Tractable Reactions to Demonstrate Kubas Binding



- 14 / 16e⁻ complex (depending on amide lone pair donation)
- Fe^{II} = d⁶ = backdonating to H₂



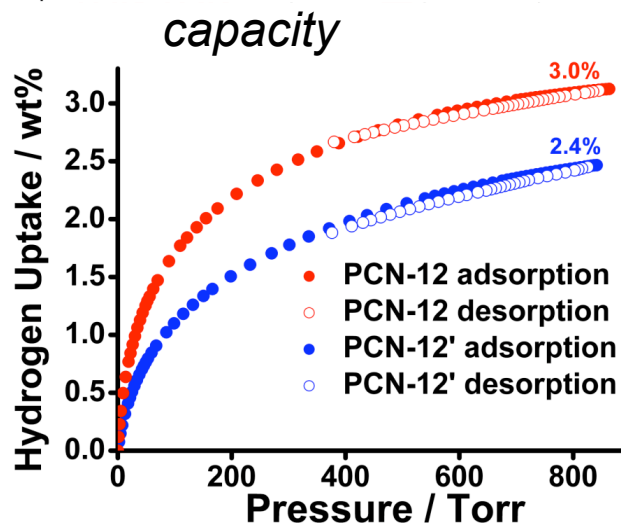
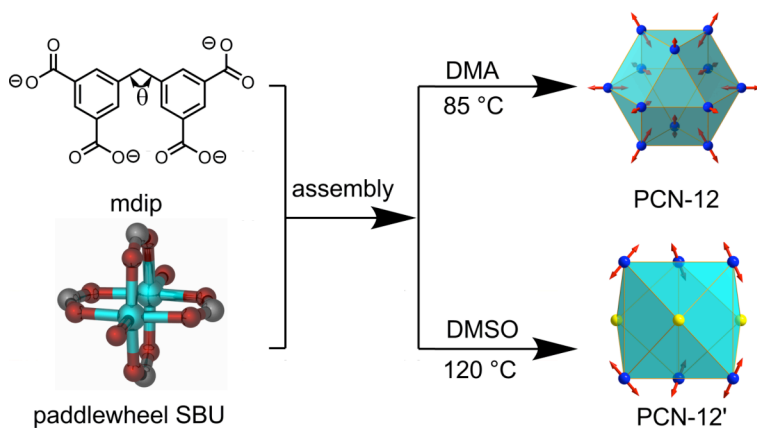
- Highly redox active at Fe and B centers
- Substitution of Cp ring may allow for H₂ binding
- Boron bridge will provide H₂ binding site



Solution NMR may be employed to rapidly determine formation of Kubas complexes.

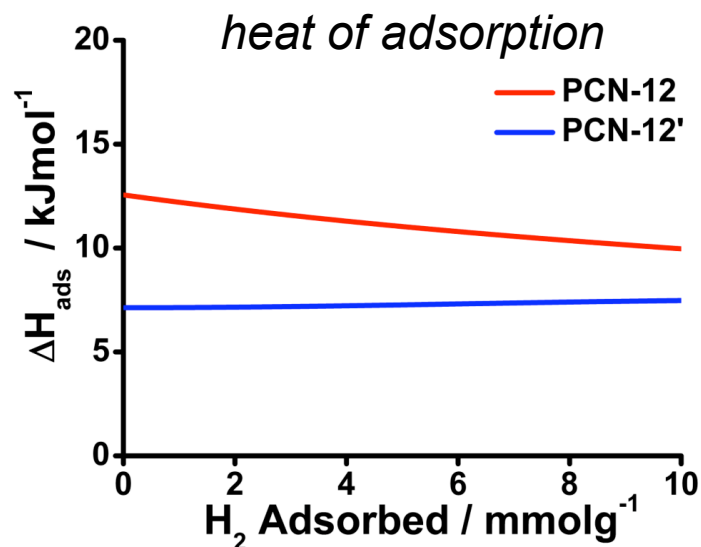


Metal Alignment in MOFs Enhances Enthalpy



PCN-12 exhibits **3.0 wt%** at 77K and 1 bar,
with a volumetric density of 24.6 mg/cm³

- Polymorphs have identical composition and atom-to-atom connectivity, but different metal alignments.
- Enhanced heat persists to relatively high coverages.
(2 H₂/Cu ~ 1.7 wt%)

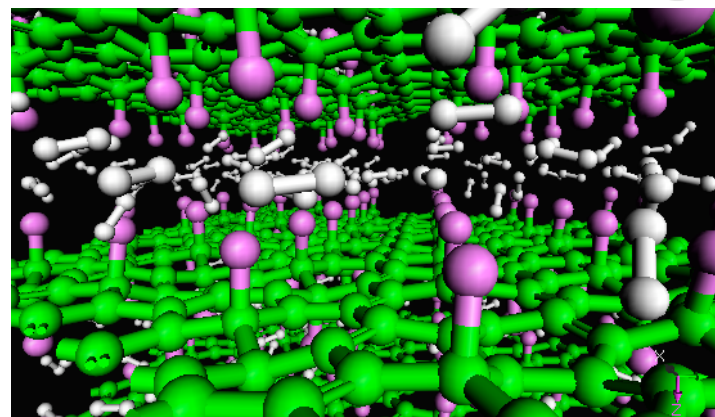
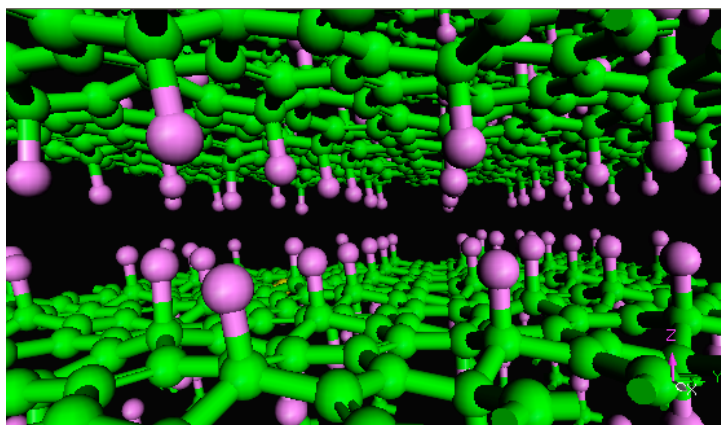


ΔH of PCN-12 is ~**12.5 kJ/mol** at low coverage, and ~**10 kJ/mol at 2 wt%**





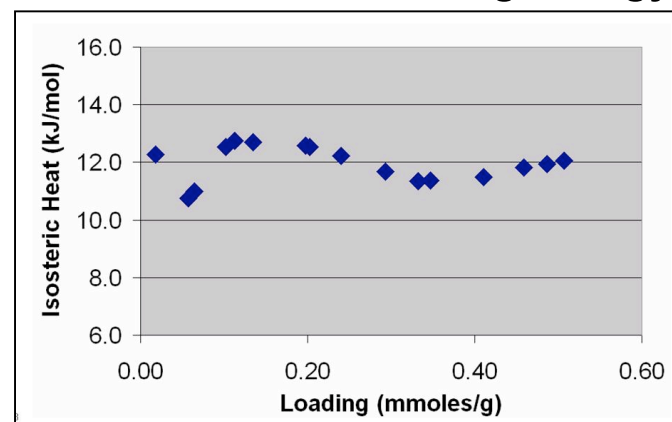
F⁻ Anion Intercalated Graphite for Enhanced Binding



Charge transfer from F⁻ to σ^* -orbital of H₂ enables enhanced binding energy

Complex	H ₂ wt. %	d (Å)	Q _F	ΔE (kJ/mol·H ₂)
C ₃₂ F ₈	-	5.698	-0.659	-
C ₃₂ F ₈ ·H ₂	0.37	5.613	-0.656	-23.3
C ₃₂ F ₈ ·2H ₂	0.74	5.602	-0.655	-19.6
C ₃₂ F ₈ ·12H ₂	4.29	6.556	-0.657	-10.5
C ₃₂ F ₈ ·24H ₂	8.22	7.723	-0.656	-3.6

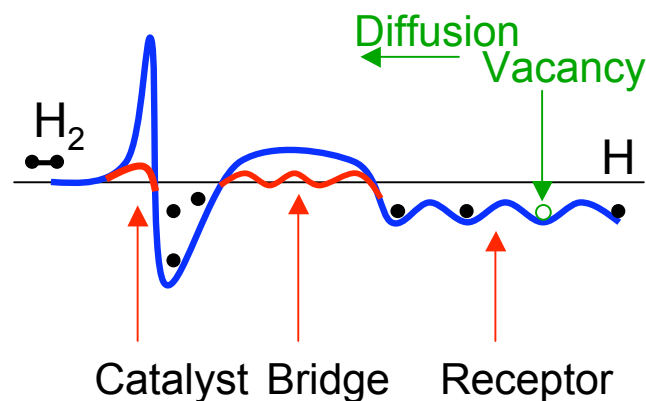
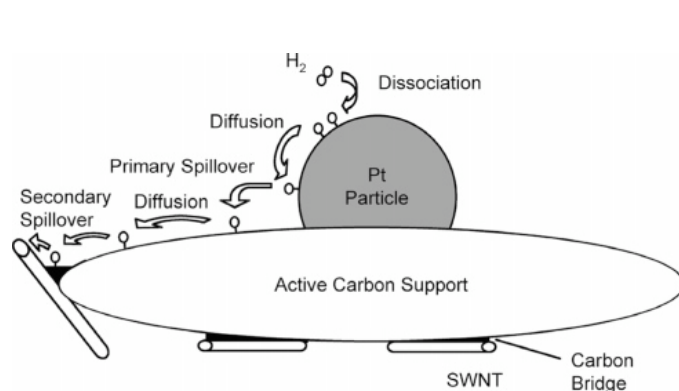
Calculated values



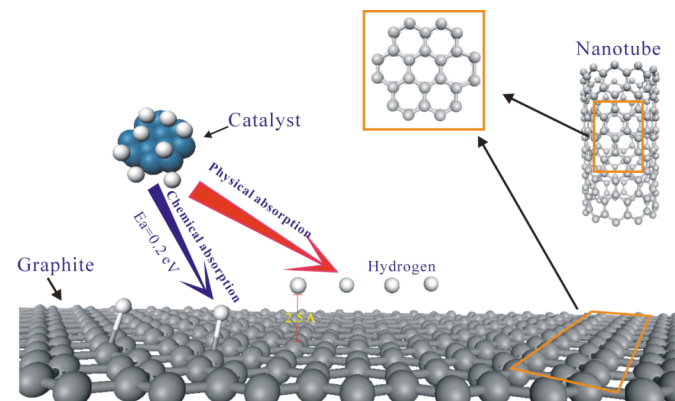
Mixed F⁻ / BF₄⁻ Intercalated Graphite



Dissociative Hydrogenation with Pt Catalyst

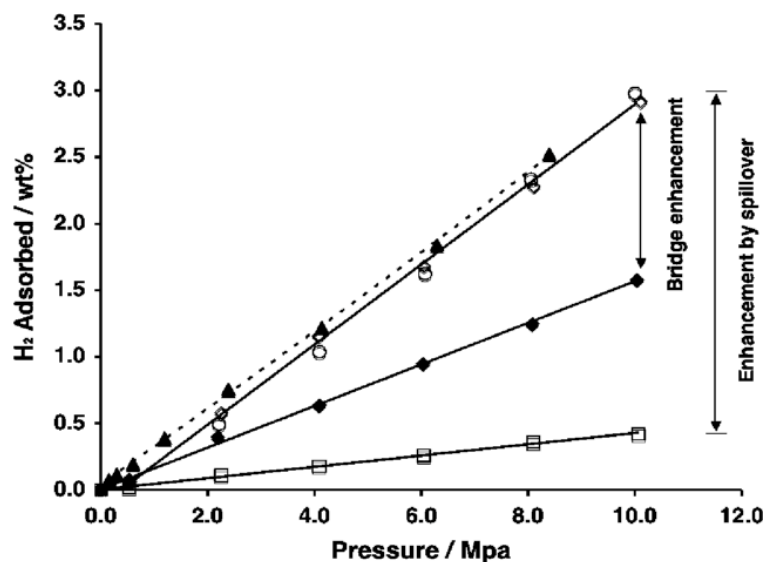


- Well dispersed Pt particles catalyze dissociative H_2 adsorption on a variety of high surface area supports including activated carbon, MOFs, carbon nanohorns and aerogels.
- Incorporation of simple bridge structures to facilitate H_2 diffusion and increased capacity.
- Process fully reversible at room temperature.

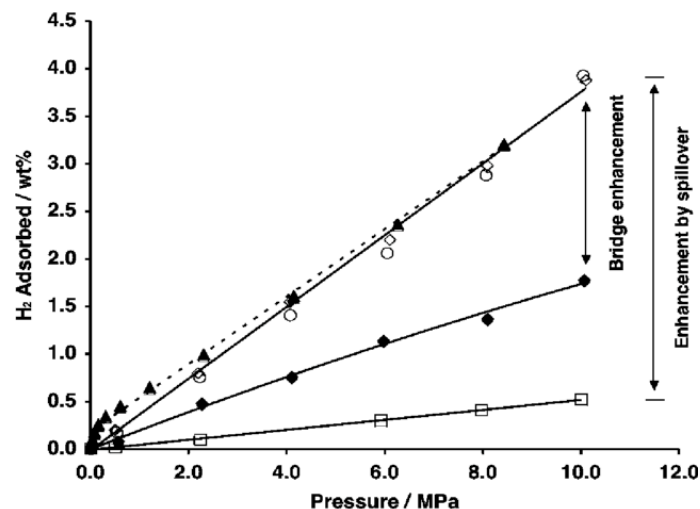




Spillover on Metal Organic Frameworks



IRMOF-1



IRMOF-8

□ Pure IRMOF

◆ with PT/AC

▲ with PT/AC and sugar bridge

Spillover is observed for MOFs with simple incorporation of Pt catalyst mixed with activated carbon and further improved with sugar bridges.

Y. Li, R.T Yang JACS 128 (2006) 8136





- **High surface area, porous high-density materials provide frameworks for hydrogen adsorption materials.**
- **Substitution of heteroatoms e.g. boron in carbon may allow for the binding energy of H₂ in frameworks to increase.**
- **Isolated metal atoms in various frameworks can also bind dihydrogen species with an enhanced binding energy.**
- **Catalytic hydrogen dissociative adsorption is reversible at room temperature with a Pt catalyst.**



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Acknowledgements

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Hydrogen, Fuel Cell, and Infrastructure Technologies
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Thank You for Your Attention